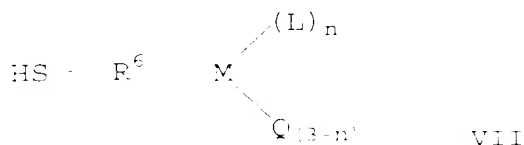


We claim:

1. In the process of producing a chemically  
 5 treated filler by contacting an acidic aqueous suspension of  
 an amorphous or particulate inorganic oxide selected from  
 precipitated silica, colloidal silica or mixtures thereof with  
 a coupling agent to form an acidic aqueous suspension of  
 chemically treated filler, optionally in the presence of a  
 10 surfactant and/or a water miscible solvent, and recovering  
 said filler, the improvement comprises using as said coupling  
 agent a combination of (a) mercaptoorganometallic compound and  
 (b) non-sulfur organometallic compound(s) in a weight ratio of  
 (a) to (b) of at least 0.05:1 in an aqueous suspension of  
 15 inorganic oxide having a pH of 2.5 or less, and treating the  
 acidic aqueous suspension of the chemically treated filler  
 with acid neutralizing agent(s) to increase the pH of said  
 suspension to a range of from 3.0 to 10.

20 2. The process of claim 1 wherein the  
 mercaptoorganometallic material is represented by the  
 following graphic formula VII:



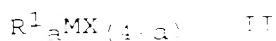
25 wherein M is silicon, L is halogen or  $-\text{OR}^7$ , Q is hydrogen,  $\text{C}_1-$   
 $\text{C}_{12}$  alkyl, or halosubstituted  $\text{C}_1-\text{C}_{12}$  alkyl,  $\text{R}^7$  is  $\text{C}_1-\text{C}_{12}$  alkylene,  
 $\text{R}^8$  is  $\text{C}_1-\text{C}_{12}$  alkyl or alkoxyalkyl containing from 2 to 12 carbon  
 atoms, said halogen or (halo) groups being chloro, bromo, iodo  
 30 or fluoro, and n is 1, 2 or 3.

3. The process of claim 2 wherein L is  $-OR''$ ,  $R''$  is  $C_1-C_3$  alkylene,  $R'$  is  $C_1-C_4$  alkyl and n is 3.

5 4. The process of claim 2 wherein the mercapto group of the mercaptoorganometallic material is blocked.

5. The process of claim 1 wherein the mercaptoorganometallic material is selected from  
10 mercaptomethyltrimethoxysilane, mercaptoethyltrimethoxysilane, mercaptopropyltrimethoxysilane, mercaptomethyltriethoxysilane, mercaptoethyltripropoxysilane, mercaptopropyltriethoxysilane, (mercaptomethyl)dimethylethoxysilane, (mercaptomethyl)methyldiethoxysilane, 3-mercaptopropyl-  
15 methyldimethoxysilane and mixtures thereof.

6. The process of claim 1 wherein the non-sulfur organometallic compound(s) is selected from the group consisting of organometallic compound(s) represented by  
20 formula II:



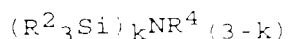
organometallic compound(s) represented by formula III:  
25



organometallic compound(s) represented by the formula IV:



organometallic compound(s) represented by formula V:



V

and a mixture of said organometallic compounds; wherein each M is independently silicon, titanium or zirconium; each R<sup>1</sup> is  
5 independently a hydrocarbon group of from 1 to 18 carbon atoms or R<sup>1</sup> is an organofunctional hydrocarbon group of from 1 to 12 carbon atoms wherein, said functionality is amino, carboxylic acid, carbinol ester, or amido; each X is independently  
10 selected from the group consisting of halogen, amino, alkoxy groups of from 1 to 12 carbon atoms and acyloxy groups of from 1 to 12 carbon atoms, a is the integer 1, 2 or 3; each R<sup>2</sup> is independently halo, hydroxy, or a hydrocarbon group containing from 1 to 18 carbon atoms with the proviso that at least 50  
15 mole percent of the R<sup>2</sup> substituents are hydrocarbon groups containing from 1 to 18 carbon atoms, c is an integer from 2 to 10,000; each R<sup>3</sup> is independently halo, hydroxy, or a hydrocarbon group containing from 1 to 18 carbon atoms and d is an integer from 3 to 20; each R<sup>4</sup> is independently hydrogen or a hydrocarbon group containing from 1 to 18 carbon atoms  
20 and k is 1 or 2; and said halo or halogen is selected from chloro, fluoro, bromo or iodo.

1. The process of claim 1 wherein the non-sulfur organometallic compound(s) is selected from the  
25 group consisting of diethyldichlorosilane, allylmethyldichlorosilane, methylphenyldichlorosilane, phenylethyldiethoxysilane, 3,3,3-trifluoropropylmethyldichlorosilane, trimethylbutoxysilane, sym-diphenyltetramethyldisiloxane, trivinyltrimethyl-  
30 cyclotrisiloxane, octamethylcyclotetrasiloxane, hexaethyldisiloxane, pentylmethyldichlorosilane, divinyl dipropoxysilane, vinyl dimethylchlorosilane, vinylmethyldichlorosilane, vinyl dimethylmethoxysilane,

trimethylchlorosilane, trimethylmethoxysilane,  
trimethylethoxysilane, methyltrichlorosilane,  
methyltrimethoxysilane, methyltriethoxysilane,  
hexamethyldisiloxane, hexenylmethyldichlorosilane,  
5 hexenyldimethylchlorosilane, dimethylchlorosilane,  
dimethyldichlorosilane, dimethyldimethoxysilane,  
dimethyldiethoxysilane, hexamethyldisilazane,  
trivinyltrimethylcyclotrisilazine, polydimethylcyclosiloxanes  
comprising 3 to about 20 dimethylsiloxyl units,  
10 tetra(C<sub>1</sub>-C<sub>18</sub>)alkoxy titanates, methyl triethoxy titanium (iv),  
methyl titanium (iv) triisopropoxide, methyl titanium (iv)  
tributoxide, methyl titanium (iv) tri-t-butoxide, isopropyl  
titanium (iv) tributoxide, butyl titanium (iv) triethoxide,  
butyl titanium (iv) tributoxide, phenyl titanium (iv)  
15 triisopropoxide, phenyl titanium (iv) tributoxide, phenyl  
titanium (iv) triisobutoxide, [Ti(CH<sub>2</sub>Ph)<sub>3</sub>(NC<sub>5</sub>H<sub>11</sub>)]  
[Ti(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(NEt<sub>2</sub>)<sub>2</sub>], tetra(C<sub>1</sub>-C<sub>18</sub>)alkoxy zirconates, phenyl  
zirconium (iv) trichloride, methyl zirconium (iv) trichloride,  
ethyl zirconium (iv) trichloride, propyl zirconium (iv)  
20 trichloride, methyl zirconium (iv) tribromide, ethyl zirconium  
(iv) tribromide, propyl zirconium (iv) tribromide,  
chlorotripentyl zirconium (iv) and mixtures of such  
organometallic compounds.

25                   8.     The process of claim 6 wherein the non-sulfur  
organometallic compound(s) is represented by formulae II, III,  
IV, V or a mixture of said organometallic compound(s) wherein  
each M is silicon.

30                   9.     The process of claim 6 wherein the non-sulfur  
organometallic compound(s) is represented by formula II  
wherein R<sup>1</sup> is C<sub>1</sub>-C<sub>6</sub> alkyl, X is chloro, a is 2 and the  
inorganic oxide is precipitated silica.

10. The process of claim 1 wherein the weight ratio of (a) to (b) is from 0.05:1 to 10:1.

5 11. The process of claim 9 wherein the weight ratio of (a) to (b) is from 0.2:1 to 2:1.

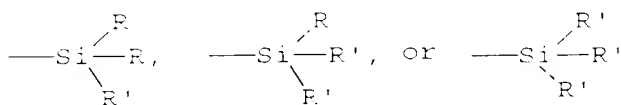
12. The process of claim 1 wherein (a) mercaptoorganometallic compound is replaced by a combination  
10 of mercaptoorganometallic compound and bis(alkoxysilylalkyl)polysulfide in a weight ratio of mercaptoorganometallic compound to bis(alkoxysilylalkyl)polysulfide of from at least greater than 1:1.

15 13. The process of claim 12 wherein the weight ratio of mercaptoorganometallic material to bis(alkoxysilylalkyl)polysulfide is from 5:1 to 50:1 and the inorganic oxide is precipitated silica.

20 14. The process of claim 12 wherein the bis(alkoxysilylalkyl)polysulfide is represented by the following graphic formula VII:

25 
$$\text{Z-alk-S}_{n'}\text{-alk-Z, VII}$$

in which alk is a divalent hydrocarbon radical having from 1 to 18 carbon atoms;  $n'$  is a whole number of 2 to 12 and Z is:



wherein R is an C<sub>1</sub>-C<sub>4</sub> alkyl or phenyl group, and R' is an C<sub>1</sub>-C<sub>4</sub> alkoxy, a C<sub>1</sub>-C<sub>4</sub> cycloalkoxy, or a C<sub>1</sub>-C<sub>4</sub> alkylmercapto group.

15. The process of claim 12 wherein
- 5 bis alkoxysilylalkyl)polysulfide is selected from the group consisting of 3,3'-bis(trimethoxysilylpropyl)disulfide, 3,3'-bis(triethoxysilylpropyl)tetrasulfide, 3,3'-bis(trimethoxysilylpropyl)tetrasulfide, 2,2'-bis(triethoxysilylethyl)tetrasulfide,
- 10 3,3'-bis(trimethoxysilylpropyl)trisulfide, 3,3'-bis(triethoxysilylpropyl)trisulfide, 3,3'-bis(tributoxysilylpropyl)disulfide, 3,3'-bis(trimethoxysilylpropyl)hexasulfide, 3,3'-bis(trioctoxysilylpropyl)tetrasulfide and mixtures
- 15 thereof.

16. A product of the process of claim 1.

17. A product of the process of claim 4.

20

18. A product of the process of claim 12.